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Oxocentered Cu(II) lead selenite honeycomb lattices hosting $Cu(I)Cl_2$ groups obtained by chemical vapor transport reactions†

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Chemical vapor transport (CVT) reactions were used to prepare three modular mixed-valent Cu(I)–Cu(II) compounds, $(Pb_2Cu^{2+}{}_9O_4)(SeO_3)_4(Cu^+Cl^2)Cl_5$ (1), $(PbCu^{2+}{}_5O_2)(SeO_3)_2(Cu^+Cl_2)Cl_3$ (2), and $(Pb_xCu^{2+}{}_{(6-x)}O_2)(SeO_3)_2(Cu^+Cl_2)K_{(1-x)}Cl_{(4-x)}$ (x = 0.20) (3). In their crystal structures chains of anion-centered ($OCu^{2+}{}_4$) and ($OCu^{2+}{}_3Pb$) tetrahedra form honeycomb-like double layers with cavities occupied by linear $[Cu^+Cl_2]^-$ groups.

Inorganic copper oxocompounds attract considerable attention due to their interesting structural and physical properties[1] as well as mineralogical and geochemical importance.[2] Of special interest are mixed-valent Cu(I)–Cu(II) systems with separate symmetrically independent monovalent and divalent copper sites due to their contrasted coordinations combined in one crystal structure. Herein we report on the synthesis and characterization of three novel Cu(I)–Cu(II) lead oxoselenite chlorides inspired by mineralogical discoveries in such unusual geological conditions as volcanic fumaroles.[2g,3] Here copper oxoselenites form from volcanic gases emanating from cooling magmatic chambers deep under the Earth's surface long after the period of eruptive activities. The formation of such Cu compounds in fumaroles provides a useful hint for their synthesis under laboratory conditions, in particular, the chemical vapor transport (CVT) method.[4] The specific feature of many Cu oxoselenites is the presence in their crystal structures of oxocentered $(\mu_4\text{–}O)Cu_4$ tetrahedral units that polymerize to form extended structural complexes.[2g,3] Likely, during these reactions the selenites and metal halides play the role of transport agents.[5] In order to reproduce natural exhalative chemistry, in this work, we investigate the formation of phases in the $PbO\text{–}Cu^{2+}Cl_2\text{–}Cu^+Cl\text{–}Cu^{2+}O\text{–}SeO_2$ system containing Pb^{2+} cations that possess stereochemically active $6s^2$ lone electron pairs favouring formation segregation of structural compartments occupied by these pairs.[6] In addition, the preference of Pb^{2+} ions for similar OPb_4 tetrahedral units is an asset for creation of more complex edifices.

Crystallographic information for three novel compounds synthesized by the CVT reaction method (Fig. 1a) is summarized in Table 1. Schematic representations of coordination environments of cations in the crystal structures of **1–3** are shown in

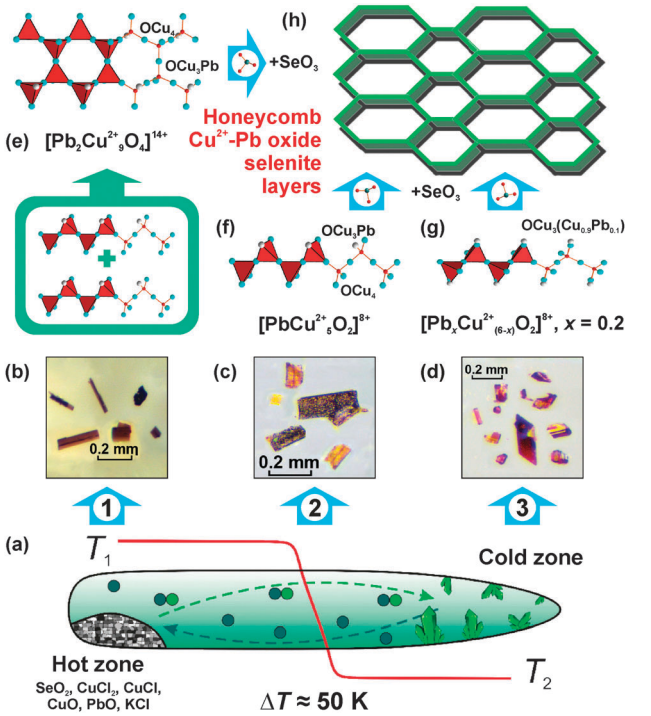

Fig. 1 General scheme of syntheses by the method of CVT reactions (a), the crystals of **1**, **2** and **3** (b–d), and the scheme of formation of honeycomb Cu^{2+}–Pb selenite layers (e–h). The types of oxo-centered 1-dimensional units (shown in red) formed by corner-sharing OCu_4 and OCu_3Pb tetrahedra in the structures of **1**, **2** and **3** are shown. (legend: Cu = cyan balls; Pb = grey balls). See text for details.

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Fig. S1, ESI.† In all the compounds, Cu^{+} cations form two relatively short Cu^{+}–Cl bonds (2.058–2.118 Å), which result in the formation of tightly bonded $[CuCl_2]^{-}$ anionic groups that can be considered as separate structural entities. The Cu^{2+} cations have mixed oxochloride coordinations that have previously been observed in Cu oxochloride compounds,[2a] with typical trends of Jahn–Teller d^9 ions. The Cu(1) and Cu(2) sites in **1**, the Cu(4) site in **2**, and Cu(3) site in **3** form $[CuO_4Cl_2]$ distorted octahedra with four short equatorial Cu–O and two long apical Cu–Cl bonds. The Cu(3) site in **1**, the Cu(2) and Cu(3) sites in **2**, and the Cu(1) site in **3** are octahedrally coordinated with $[CuO_3Cl]$ squares complemented by two long Cu–Cl bonds. The Cu(4) site in **1** forms a $[CuO_4Cl]$ trigonal bipyramid, whereas the Cu(1) site in **2** and the Cu(4) site in **3** form $[CuO_3Cl_2]$ trigonal bipyramids. The Pb atoms have asymmetrical coordinations consisting of three strong Pb–O bonds (2.356–2.420 Å) located in one coordination hemisphere and four long Pb–Cl in another. This coordination of Pb^{2+} cations is typical for lead oxohalide compounds[7] and is consistent with the presence of stereoactive lone electron pairs. In all the compounds under consideration, Se^{4+} cations form standard $(SeO_3)^{2-}$ selenite triangular pyramidal oxo-anions (Se–O = 1.688–1.726 Å). The structure of **3** has one symmetrically independent K site with the site-occupation factor (s.o.f.) equal to 0.8. Its coordination polyhedron can be described as a distorted hexagonal bipyramid. Bond-valence sums[8] calculated for all the sites in the crystal structures of **1–3** are in full agreement with their expected oxidations states (in valence units): Cu^{+} sites – 1.00–1.16, Cu^{2+} sites – 1.96–2.14, Pb^{2+} sites – 1.95–1.96, Se^{4+} sites – 4.03–4.16, and K^{+} site – 0.80.

The high variability of cation coordinations in the structures of **1–3** makes their uniform description in terms of cation coordination polyhedra a difficult task. It is therefore more reasonable to look for more mundane consideration, *e.g.* in terms of cation arrays or coordination of anions.[9] In addition to the O atoms associated with the SeO_3 groups, all three compounds contain additional O_a atoms (oxo-anions) not bonded to Se^{4+} cations and tetrahedrally coordinated by four metal atoms (Cu and Pb). In the crystal structure of **1** there are two additional O atoms, O(2) and O(4), that form $(OCu^{2+}{}_3Pb)$ and $(OCu^{2+}{}_4)$ tetrahedra, respectively. The oxo-centered tetrahedra share common corners to form $[O_4Pb_2Cu^{2+}{}_9]^{14+}$ double chains depicted in Fig. 1e. These chains are growing parallel to the *b*-axis, and its common value for the three compounds ($b \sim 6.2$ Å) denotes similar arrangement between the oxo-centered building units in the full series. These types of chains of anion-centered tetrahedra are original and have not been observed in inorganic compounds previously. The SeO_3 groups are attached to the triangular bases of oxo-centered tetrahedra that results in the formation of complex 1-dimensional $\{[O_4Pb_2Cu^{2+}{}_9](SeO_3)_4\}^{6+}$ interconnected *via* Pb–O bonds in 2-dimensional metal-oxide double layers (Fig. 2b). The projection of the layers in the (*bc*) plane leads to a honeycomb-like lattice of tetrahedra, even though this idealized vision neglects the disconnections occurring at the oxocentered-oxoanion contacts. In contrast, monometallic $[O_2Cu_5]$ honeycomb-layers are reported in several compounds based upon anion-centered tetrahedra.[9] The layers are surrounded by Cl^{-} anions in the interleaves and accommodate both linear $[Cu^{+}Cl_2]^{-}$ anions and Cl^{-} ions in the larger and smaller honeycomb-windows, respectively. The interactions between the Cl^{-} ions of the $[Cu^{+}Cl_2]^{-}$ groups and host cationic networks are restricted to rather weak Cu^{2+}–Cl^{-} (>2.975 Å), Pb^{2+}–Cl^{-} (>3.396 Å) and K^{+}–Cl^{-} (>3.478 Å) bonds with bond-valences not exceeding 0.08 valence units (Tables S1–S3, ESI†). Taking into account the relative strength of the Cu^{+}–Cl bonds and weak interactions between them and the rest of the structure, these units may be considered as guest anions embedded in the complex metal oxochloride matrix based upon anion-centered tetrahedra.

A very similar 'host–guest' principle is at work in the structures of **2** and **3** as well. Here the $(OCu^{2+}{}_3Pb)$ and $(OCu^{2+}{}_4)$ tetrahedra share corners to produce single chains extending along the common *b*-parameter that have $[O_2PbCu_5]^{8+}$ and $[O_2Pb_xCu^{2+}{}_{(6-x)}]^{8+}$

Table 1 Crystallographic data for **1**, **2**, and **3**

	1	**2**	**3**
Empirical formula	$(Pb_2Cu^{2+}{}_9O_4)(SeO_3)_4(Cu^{+}Cl_2)Cl_5$	$(PbCu^{2+}{}_5O_2)(SeO_3)_2(Cu^{+}Cl_2)Cl_3$	$(Pb_xCu^{2+}{}_{(6-x)}O_2)(SeO_3)_2(Cu^{+}Cl_2)K_{(1-x)}Cl_{(4-x)}$, $x = 0.20$
Crystal system		*C*2/*m*	
Space group		Monoclinic	
a (Å)	18.605(17)	18.4956(4)	15.116(1)
b (Å)	6.204(6)	6.1454(1)	6.1850(4)
c (Å)	12.673(11)	15.2985(4)	9.2672(9)
β (deg)	109.87(2)	119.311(1)	95.965(5)
V (Å^3)	1376(2)	1516.25(6)	861.72(12)
ρ_{calc} (g cm^{-3})	4.514	4.607	3.840
μ (mm^{-1})	25.78	25.02	15.52
Reflection collected	7722	6910	4817
Independent reflections (R_{int})	1301 (0.069)	1924 (0.024)	974 (0.029)
Goodness-of-fit	0.791	1.231	1.121
$R_1[I > 2\sigma(I)]^a$	0.0257	0.0260	0.0412
wR_2	0.0349	0.0761	0.1172
R_1 (all data)	0.0475	0.0267	0.0496
wR_2	0.0378	0.0761	0.1176
Largest diff. peak and hole [e Å^{-3}]	0.951, −0.988	3.783, −2.942	4.244, −1.592

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)_2]/\sum[w(F_o^2)^2]\}^{1/2}$.

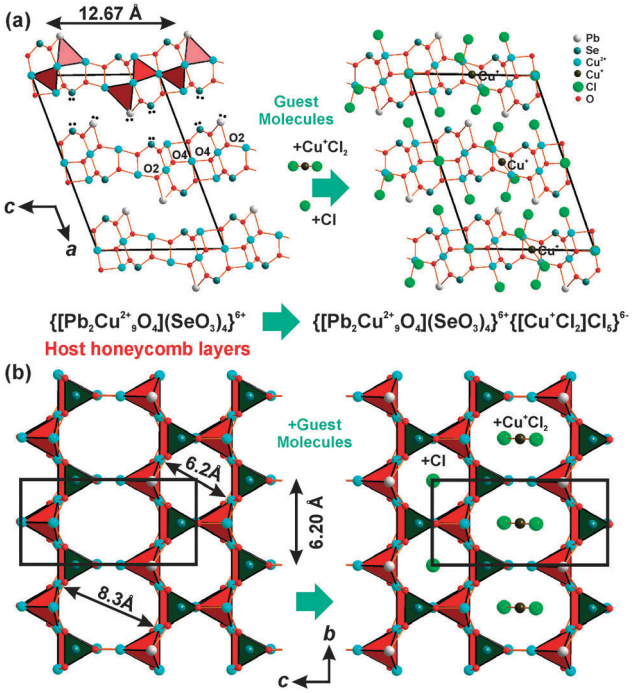

Fig. 2 General projections of the structure of **1** along the *b* and *a* axes – (a) and (b). Honeycomb layers of $\{[Pb_2Cu^{2+}{}_9O_4](SeO_3)_4\}^{6+}$ composition are hosts for the $[Cu^+Cl_2]^-$ guest species localized in the layer cavities. The $\{[Pb_2Cu^{2+}{}_9O_4](SeO_3)_4\}^{6+}$ layers are formed *via* interconnection of the $[Pb_2Cu^{2+}{}_9O_4]$ oxo-centered chains (red) and isolated SeO_3 groups (dark-green). The O(2) and O(4) designated in (a) are central oxygen atoms in OCu_4 and OCu_3Pb tetrahedra, respectively.

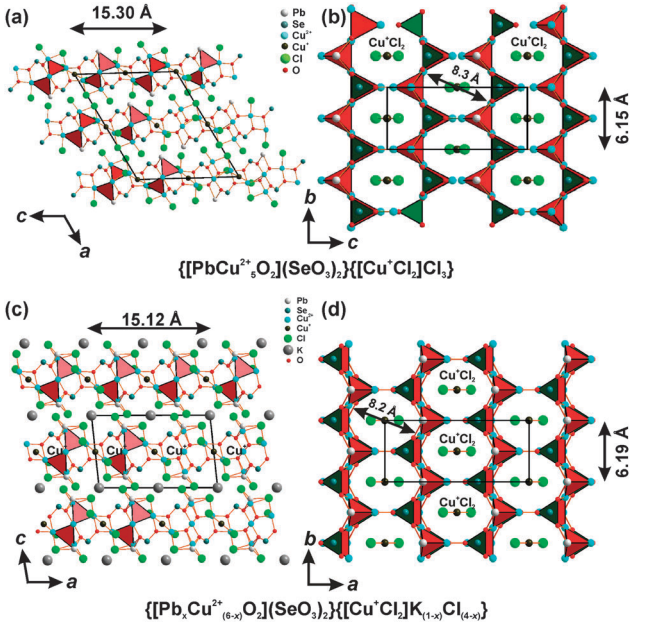

Fig. 3 General projections of the structure of **2** (a, b) and **3** (c, d). In **2**, the OCu_4 and OCu_3Pb tetrahedra (red) form single $[O_2PbCu_5]$ chains, which results in the enlargement of the *c*-parameter value from 12.67 Å (in **1**) to 15.30 Å (in **2**). In **3**, K atoms are located in the interlayer under and above the pseudohexagonal voids filled by the $[Cu^+Cl_2]$ groups. The layers (b, d) are characterized by only one type of pore with 8.3 Å and 8.2 Å diameter in **2** and **3**, respectively.

compositions, respectively (Fig. 1f and g). Together with SeO_3 groups, these chains form 1-dimensional $\{[O_2M_6](SeO_3)_2\}^{4+}$ metal-oxide (M = Cu or Pb) backbones of the structures that are arranged to form pseudo honeycomb layers. Due to the elementary single-chains, only large honeycomb windows are created that accommodate the $[Cu^+Cl_2]^-$ guest anions (Fig. 3) as observed in **1**. The structure of **3** contains additional K^+ cations located in the interlayer space between the metal oxoselenite chloride layers. In all three structures, lone electron pairs on the Pb^{2+} and Se^{4+} cations are oriented toward the interlayer space, thus conforming the 'chemical scissor' principle of structural organization in compounds with lone-electron-pair cations.[10]

It is noteworthy that compounds **1** and **2** are closely chemically related, which can be described by the equation:

$$(Pb_2Cu^{2+}{}_9O_4)(SeO_3)_4(Cu^+Cl_2)Cl_5\ (\mathbf{1}) + Cu^+Cu^{2+}Cl_3 \rightarrow 2(PbCu^{2+}{}_5O_2)(SeO_3)_2(Cu^+Cl_2)Cl_3\ (\mathbf{2})$$

From the structural viewpoint, transition from **1** to **2** is associated with the reconstruction of the metal-oxide backbone, *i.e.* in depolymerization of anion-centered tetrahedra and splitting of the double $[O_4Pb_2Cu^{2+}{}_9]^{14+}$ chains into single $[O_2PbCu_5]^{8+}$ chains. This kind of structural reconstruction accompanied by the inclusion of imaginary ionic component $Cu^+Cu^{2+}Cl_3$ into the metal-oxide matrix is in good agreement with the principle of dimensional reduction.[11] It should also be noted that **2** is a synthetic analogue of allochalcoselite, the mineral first described to be obtained from volcanic fumaroles of the Tolbachik volcano (Kamchatka peninsula, Russia).[3d]

To summarize, three novel Cu^{2+}–Cu^+ Pb oxoselenite chlorides were obtained by the chemical vapor transport reactions, which proves the efficiency of this method for the synthesis of new mixed Cu^{2+}–Cu^+ based oxyhalide compounds. These compounds described herein are based upon oxocentered mixed Pb–Cu^{2+} one-dimensional units of different architectures. These units determine basic topologies of the structures and influence their stability and properties. For instance, in the three compounds only corner-sharing OCu_4 and OCu_3Pb are found in chains and double chains forming hollow voids. It follows that in all the compounds, the role of the tightly bonded $[Cu^+Cl_2]^-$ anions is that of guest complexes incorporated inside metal oxide chloride units. The present study also points out that the Cu^+Cl_2 groups may serve as transport agents of Cu^+ in Cl-rich gaseous environments such as that observed in natural volcanic fumaroles.

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